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# Infrared Spectroscopy for the Determination of Hydrocarbon Types in Jet Fuels

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# INFRARED SPECTROSCOPY FOR THE DETERMINATION OF HYDROCARBON TYPES IN JET FUELS

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## SUMMARY

The concentration of hydrocarbon types in conventional jet fuels and synfuels can be measured using a computerized infrared spectrophotometer. The computerized spectrophotometer is calibrated using a fuel of known aromatic and olefinic content. Once calibration is completed, other fuels can be rapidly analyzed using an analytical program built into the computer. The concentration of saturates can be calculated as 100% minus the sum of the aromatic and olefinic concentrations. The analysis of a number of jet fuels produced an average standard deviation of 1.76% for aromatic types and one of 3.99% for olefinic types. Other substances such as oils and organic mixtures can be analyzed for their hydrocarbon content.

## INTRODUCTION

A fuels characterization program is presently being conducted at NASA Lewis Research Center. As part of this program, the major properties of the conventional jet fuels as well as many synfuels are being investigated. This paper will discuss, in particular, a new method for determining hydrocarbon types in these fuels.

A measurement of the hydrocarbon types, aromatic and olefinic, in a petroleum product will indicate whether that product is suitable for use as a fuel or as a raw material for further processing. For example, a petroleum product with a high aromatic content would not be considered suitable for use as a fuel. This is because large amounts of aromatics will cause a fuel to combust with a smoky, sooty flame. This will tend to form troublesome deposits in aircraft engines. For many years, analysts have used the ASTM Fluorescent Indicator Adsorption (FIA) Method D1319 (ref. 1) to determine aromatics, olefins and saturates in fuels. The FIA method uses a small glass adsorption column, packed with activated silica gel, and a small amount of a fluorescent-dye mixture. The fuel sample is passed down the column, under pressure, with isopropyl alcohol as the eluent. The hydrocarbons are separated into their functional types, aromatics, olefins and saturates, according to their adsorption affinities. The fluorescent dyes complex with the functional groups creating the zones between the aromatics, olefins and saturates, that can be measured under ultraviolet light. The FIA method is specific for fuels that distill below 600° F (315.56° C). Therefore, errors may be introduced into the results when higher distilling and more highly colored fuels such as JP-5, Paraho fuels, Solvent Refined Coal (SRC) fuels, certain Diesel fuels, TOSCO Shale Oils and Experimental Referee Broadened Specification (ERBS) fuels are analyzed. The FIA method is also time consuming, taking about two hours for an analysis including packing and cleanup of the column.

A faster analytical method was needed to handle the large volume of samples being received. An investigation into the molecular structures of the aromatics and olefins in these fuels revealed that they have distinctive bonds that absorb strongly in the infrared region. Specifically, these are the C=C linkages of the benzene structure, that make up a large portion of the aromatic fraction, and the -CH=CH(trans), CH out-of-plane deformation of the bonds in the olefinic fraction.

This paper will discuss a method whereby a computing infrared spectrophotometer, such as the Beckman Microlab 620 MX Computing Infrared Spectrophotometer (fig. 1), can be programed to measure the concentration of aromatics and olefins in a fuel. The amount of saturates can then be computed from 100% minus the sum of the aromatic and olefinic concentrations.

Studies have shown (ref. 2) that aromatics have a strong absorption in the infrared region of  $1620\text{ cm}^{-1}$  to  $1605\text{ cm}^{-1}$  while the olefins absorb strongly in the region of  $1005\text{ cm}^{-1}$  to  $960\text{ cm}^{-1}$ . In this study the exact wavenumbers used for the aromatic peak were  $1615\text{ cm}^{-1}$  and  $1605\text{ cm}^{-1}$ . The wavenumber  $1615\text{ cm}^{-1}$  was used for all Jet-A fuels and other lightly colored fuels. The second wavenumber,  $1605\text{ cm}^{-1}$ , was used for the dark colored SRC fuels. These fuels had to be diluted with carbon tetrachloride ( $\text{CCl}_4$ ) before they could be analyzed due to the dark color and high concentration of aromatics. The shift in wavenumbers that occurred could be due to the dilution with  $\text{CCl}_4$ , the dark color of the fuel or its completely different characteristics. The exact wavenumbers used for the olefinic peak were  $1005\text{ cm}^{-1}$  and  $970\text{ cm}^{-1}$ . The  $970\text{ cm}^{-1}$  wavenumber was used for the Jet-A and lighter colored fuels while  $1005\text{ cm}^{-1}$  was used for the SRC fuels.

Due to the lack of a standard reference fuel with a known aromatic and olefinic content; a conventional Jet-A fuel was used as a calibration standard for the infrared spectrophotometer and the accompanying computer. Jet-A fuel was chosen over the other types of jet fuels because reproducible results have consistently been obtained using the FIA method. The standard fuel as well as the other samples were also analyzed using the FIA method to obtain comparisons between hydrocarbon concentrations. The standard deviations, based on an average of five infrared determinations of the standard Jet-A fuel sample, are 0.57% and 2.41%, respectively, for aromatics and olefins. These results are much less than the results of 1.87% for aromatics and 20.49% for olefins, computed from the FIA results.

#### APPARATUS AND MATERIALS

##### FIA METHOD - APPARATUS AND MATERIALS

1. Precision-Bore Glass Adsorption Column.
2. Ultraviolet Light Source.
3. Hypodermic Syringe, 1 ml graduated to 0.01 ml.

##### REAGENTS

1. Silica Gel, 100 to 200 mesh.
2. Fluorescent Indicator Dyed Gel.
3. Isopropyl Alcohol, Certified A.C.S.



## INFRARED SPECTROSCOPY METHOD - APPARATUS AND MATERIALS

1. Beckman Microlab 620 MX Computing Infrared Spectrophotometer.
2. KBr Liquid Infrared Cells, pathlength of 0.212 mm for the sample cell and 0.213 mm for the reference cell.
3. Hypodermic Syringe, 1 ml.

### REAGENTS:

1. Carbon Tetrachloride ( $\text{CCl}_4$ ), Certified A.C.S.

### FUEL SAMPLES

1. Jet-A Fuels, 5 different samples.
  - a. #1 Jet-A, used as a standard for light colored fuels.
  - b. L-1 Jet-A.
  - c. #104 Jet-A.
  - d. #106 Jet-A.
  - e. 5B Jet-A.
2. #2 Diesel Fuel.
3. Experimental Referee Broadened Specification Fuel (ERBS-GE).
4. JP-4 Fuel.
5. Solvent Refined Coal Fuels, 2 different samples.
  - a. SRC-II, used as a standard for dark colored fuels.
  - b. SRC.

### PROCEDURE

A Jet-A fuel, designated as #1 Jet-A, was used as the standard fuel to calibrate the infrared spectrophotometer and its computer for all fuels except the Solvent Refined Coal fuels. This standard fuel was first analyzed using the FIA method. The hydrocarbon concentrations found were 17.78% aromatics, 0.37% olefins and 81.82% saturates; these results were not normalized to 100%.

The standard fuel was then injected into a KBr liquid cell, with a pathlength of 0.212 mm, and placed into the sample compartment of the infrared spectrophotometer. A 6.5 minute routine scan was run on the sample to determine that the exact absorption peak for the aromatics is at  $1615\text{ cm}^{-1}$  and that the olefinic peak is at  $970\text{ cm}^{-1}$ . Background frequencies of  $1643\text{ cm}^{-1}$ ,  $1579\text{ cm}^{-1}$  and  $1578\text{ cm}^{-1}$  for the aromatic peak and  $995\text{ cm}^{-1}$ ,  $955\text{ cm}^{-1}$  and  $954\text{ cm}^{-1}$  for the olefinic peak were also selected from this spectral scan (fig. 2). These background frequencies, which bracket the analytical frequencies, were used by the computer for baseline corrections (ref. 3).

The computing portion of the infrared spectrophotometer was calibrated by inserting these frequencies, the cell pathlength, FIA determined hydrocarbon concentrations of #1 Jet-A fuel and other information into the built-in quantitative analysis routines. These routines are summarized as follows (ref. 4):

1. The POINT PROGRAM uses three basepoint frequencies for baseline construction to compute net absorbance values. The program also calls for one analytical frequency for each component to be analyzed.

2. The NORMALIZE PROGRAM then converts all percent transmission values to absorbance, normalizes them for cell pathlength (0.212 mm) and component concentration (17.8% aromatics and 0.37% olefins).

3. The ARRAY BUILD PROGRAM then arranges the analytical data in matrix form, as a series of simultaneous equations; one equation for each component. The matrix that is developed for each program is then inverted and the calibration process is completed.

4. The ANALYSIS PROGRAM, which uses the results computed in the Array Build Program, is then used to determine the aromatic and olefinic concentrations of the samples.

Once the infrared spectrophotometer (IR) and the accompanying computer were calibrated, five independent samples of the standard #1 Jet-A fuel were analyzed. When the aromatic and olefinic concentrations were determined, they were summed and this value was subtracted from 100% to yield the saturate concentration. The four other Jet-A fuels were analyzed in like manner.

The analysis of the three other light colored fuels required the insertion of a correlation factor in the Analysis Program. This factor was calculated from the following expression:

$$\frac{\text{Percent Hydrocarbon Found}}{\text{Percent Hydrocarbon Known}} \times \text{Pathlength of Cell (ref. 4)}.$$

In other words, the factor is the result of dividing the percentage aromatics or olefins found using the IR Analysis Program calibrated with #1 Jet-A, by the percentage determined using the FIA method. This value is multiplied by the pathlength of the cell. This correlation factor is inserted when the computer calls for the pathlength in the Analysis Program.

The Solvent Refined Coal fuels posed a problem in the analysis because of their large aromatic content and dark color. The aromatic peaks were so large that they went off scale. To solve this program, the samples were diluted in the ratio of 30% fuel to 70% CCl<sub>4</sub>. This reduced the aromatic peaks to a measurable level and lightened the color of the fuels.

A shift in the aromatic and olefinic peaks, from 1615 cm<sup>-1</sup> to 1605 cm<sup>-1</sup> and from 970 cm<sup>-1</sup> to 1005 cm<sup>-1</sup>, respectively, also occurred. It is not known if this was due to the dilution of the samples or because the Solvent Refined Coal fuels have different characteristics relative to the other fuels or because of their dark color. Whatever the cause, the #1 Jet-A fuel could no longer be used as a calibration standard, so SRC-II fuel was used instead. The sample was diluted to 30% with CCl<sub>4</sub> and the calibration procedure was carried out in the same way as was done for the #1 Jet-A sample. The only differences were that CCl<sub>4</sub> was placed in the reference beam of the spectrophotometer and the new frequencies and concentrations, as determined by the FIA method, were inserted into the calibration programs. Carbon tetrachloride was placed in the reference beam of the spectrophotometer to eliminate the CCl<sub>4</sub> spectrum from the sample spectrum because one CCl<sub>4</sub> peak appeared at the same frequency, 1005 cm<sup>-1</sup>, as the olefinic peak.

To repeat, all standards and samples were analyzed a total of five times and these results are discussed in the next section. All of the fuels were also analyzed three times each, using the ASTM Fluorescent Indicator Adsorption Method D1319. When the two Solvent Refined Coal Fuels were analyzed using the FIA method, they were tested without the CCl<sub>4</sub> dilution. All of these results were used for comparison purposes to determine the accuracy of the Infrared method.



## RESULTS AND DISCUSSION

A comparison of the results of the ASTM-FIA D1319 method and the infrared spectroscopy method is given in table 1. It can be seen that the two sets of results, especially for the aromatic content, agree quite favorably with one another. The larger discrepancies between the two sets of olefinic concentrations for the Jet-A fuels could be due to the difficulty in determining the exact olefinic zone on the FIA column. When the olefinic content of a fuel is 0.5% or less, the zone on the FIA column is only 0.3 mm to 0.5 mm wide and there can be an 0.1 mm error made in measurement because the average width of the grease pencil mark, made to indicate the boundaries, can be 0.1 mm. A 0.1 mm change in the olefinic band can cause a large change in the concentration when such small amounts are being measured. Another problem is that the olefinic band is said to be the bright yellow region in a paler yellow region. The differentiation of bright yellow from pale yellow is a subjective judgment that can also introduce errors.

There is a large difference in the results between the methods when the hydrocarbon concentrations of the Solvent Refined Coal fuels are compared. The obvious reason for this is the dark color of the fuels. Since these fuels were not diluted with  $\text{CCl}_4$  when they were analyzed by the FIA method, the dark coloration masked the various zones and caused a bleeding of the aromatic zone. This made measurement of the zones difficult so that when the hydrocarbon concentrations were computed, the results may not have been as accurate as those of the lighter colored fuels.

A comparison of the standard deviations calculated for both methods is given in table 2. On the average, the infrared method has a much lower standard deviation than the FIA method. This would indicate that the infrared spectroscopy method yields more precise results than the FIA method and that these results are just as accurate.

## CONCLUSIONS

To summarize, computerized infrared spectroscopy is a rapid, sensitive and accurate method to determine the concentrations of hydrocarbon types in conventional jet fuels. The dark coloration of some synfuels is a property that interferes with this method. More research in this area is needed to insure that accurate results are being obtained.

This method also lends itself to the analysis of other substances such as oils and hydrocarbon mixtures that cannot be easily analyzed using the FIA methods.

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TABLE 1 - COMPARISON OF RESULTS BETWEEN FIA  
AND INFRARED METHODS

Sample	Aromatics %		Olefins %		Saturates %	
	FIA	IR	FIA	IR	FIA	IR
#1 Jet-A	17.78	17.98	0.37	0.36	81.82	81.66
L-1 Jet-A	15.57	15.80	.59	.31	83.84	83.89
#104 Jet-A	12.98	11.53	.59	.35	86.46	88.12
#106 Jet-A	14.53	14.99	.63	.34	84.92	84.67
5B Jet-A	15.47	16.07	.45	.30	84.06	83.63
#2 Diesel	23.53	23.48	.62	.64	75.72	75.88
ERBS-GE	28.48	26.01	.47	.47	70.97	73.52
JP-4	12.83	12.20	.62	.60	86.55	87.20
SRC-II	*82.75	89.62	*2.05	2.17	*15.15	8.21
SRC	*73.41	72.21	*5.86	1.55	*20.27	26.24

\*Samples analyzed without CCl<sub>4</sub> dilution.  
Results not normalized to 100%<sup>4</sup>.

TABLE 2 - STANDARD DEVIATIONS FOR FIA  
AND INFRARED METHODS

Sample	$\sigma_s$ Aromatics		$\sigma_s$ Olefins	
	FIA	IR	FIA	IR
#1 Jet-A	1.87	0.57	20.49	2.41
L-1 Jet-A	1.11	.45	15.39	1.61
#104 Jet-A	1.21	.61	24.12	1.43
#106 Jet-A	2.48	.47	23.41	1.47
5B Jet-A	3.45	.17	11.22	1.67
#2 Diesel	10.17	.37	5.82	1.75
ERBS-GE	5.73	.36	11.85	2.81
JP-4	.30	2.29	5.23	3.33
SRC-II	1.31	5.20	15.68	14.85
SRC	1.09	3.54	16.45	5.04
Average $\sigma_s$	2.87	1.76	14.97	3.99





Figure 1. - General view of the instrument.

- |   |                               |
|---|-------------------------------|
| 1. - Digital display and status display | 6. - Sample compartment cover |
| 2. - Keyboards                          | 7. - Printer                  |
| 3. - Manual chart drive knob            | 8. - Disk drives (1 and 0)    |
| 4. - Chart paper                        | 9. - Compuset                 |
| 5. - 100%T adjust knob                  |                               |

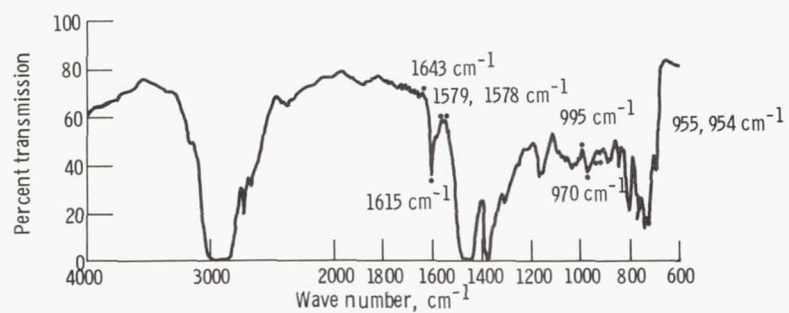


Figure 2. - Infrared spectrum of #1 Jet-A fuel.

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